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LMSC GLASS-LIKE CARBON

GLASS-LIKE CARBONS TAILORED FOR SPECIFIC REQUIREMENTS

- STANDARD GLASSY CARBON—GRADES 2000 AND 3000
- HIGH-STRENGTH GLASSY CARBON—GRADES 2000 AND 3000
- HIGH-CONDUCTIVITY GLASSY CARBON—GRADE 2500

Lockheed

PALO ALTO RESEARCH LABORATORY

LOCKHEED MISSILES & SPACE COMPANY • A GROUP DIVISION OF LOCKHEED AIRCRAFT CORPORATION
PALO ALTO, CALIFORNIA

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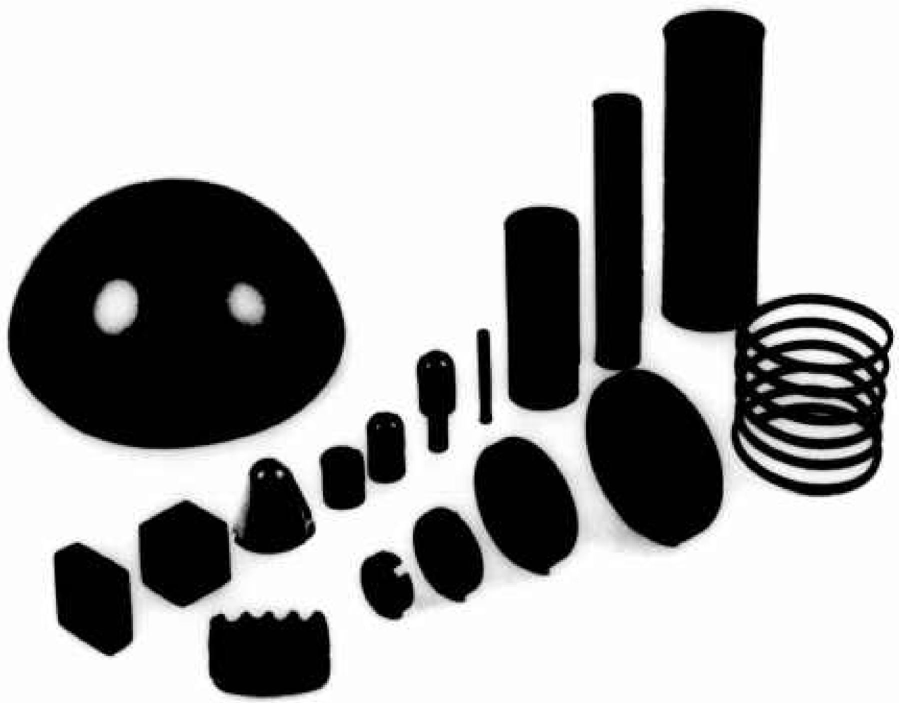

Typical Shapes of LMSC Glass-Like Carbon

LMSC GLASS-LIKE CARBON

Glass-Like Carbons Tailored For Specific Requirements

- Standard Glassy Carbon – Grades 2000 and 3000
- High-Strength Glassy Carbon – Grades 2000 and 3000
- High-Conductivity Glassy Carbon – Grade 2500

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FOREWORD

LMSC Glass-Like Carbon* was developed in 1967 by the Lockheed Palo Alto Research Laboratory of Lockheed Missiles & Space Company, Palo Alto, California. Since that time, we have developed a very high-strength glassy carbon known as the A-2 series and a graphite-modified glassy carbon with high thermal and electrical conductivity.

This brochure is to familiarize interested personnel with the properties of this new form of carbon. The conventional grades of glass-like carbon have advanced from the basic development phase to the prototype and production stage. The two newer types of glass-like carbon are available as special items. They have not yet been as completely characterized or developed as the parent material.

Material and additional information may be obtained by contacting Wanda G. Bradshaw or Patrick C. Pinoli, (415) 324-3311, Ext. 45271, Lockheed Palo Alto Research Laboratory, 3251 Hanover Street, Palo Alto, California 94304.

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*Patent applied for, Lockheed.

INTRODUCTION

LMSC Glass-Like Carbon is one of the newer forms of hard, impervious, and nongraphitizing-type carbons. It is a monolithic form of carbon produced from the degradation of an organic polymer. The precursor polymer employed can be modified substantially to produce variations in the carbon structure. The carbon end use is analyzed to determine the best precursor resin.

The property similarities between this material and glass are high tensile strength, high compressive strength, low permeability, isotropic characteristics, and low impact strength. However, since the material is a pure carbon, the high-temperature properties are substantially higher than those of glass. Tensile strength at 2500°C is double the room temperature values. Preliminary studies indicate long-term stability at 1000°F in air. As a new high-temperature structural material and an improved carbon product, LMSC Glass-Like Carbon offers many advantages. Current applications include high-temperature reaction vessels, crucibles, resistance elements, induction susceptors, and electrodes. The following paragraphs will review fabrication process, design engineering, and property analysis.

FABRICATION PROCESS

The fabrication of LMSC Glass-Like Carbon involves a thermosetting organic resin preparation, molding to shape, and a pyrolysis operation. Shapes are produced to net dimension by incorporating a uniform shrinkage factor into the mold design. Two grades of material are produced, 2000 and 3000. These grade numbers refer to the maximum heat-treatment temperature in degrees centigrade to which the material has been conditioned. The maximum use temperature is not related to these heat-treatment temperatures. The 3000-grade material offers a higher thermal conductivity with some loss in mechanical properties.

Fabrication time obviously depends on the required shape and work load; however, as a guide line, simple shapes can be produced in 6 weeks while more complex shapes, with close tolerances, require 12 weeks.

DESIGN ENGINEERING

A design limitation of 1/8-in. thickness is recommended at this time. This is not rigid, however, since 1/5-in. thick material is being produced, and in advanced studies 3/8-in. thick material has been produced. Shell composite structures are being evaluated for such applications as nose tip and rocket nozzle configurations.

Where thick carbon bodies with a glassy carbon shell are desired, the use of conventional graphite for a substructure has proved successful. The thermal expansion of LMSC Glass-Like Carbon can be closely matched with a conventional high-density polycrystalline graphite. Structural attachment using epoxy adhesives and phenolics is excellent. Molding or machining threads into the precursor shape prior to pyrolysis provides excellent load transfer with low production costs. Maximum part size is limited by our pyrolysis furnace size which is a vertical-tubular shape 8 in. in diameter by 10 in. high. The frontispiece illustrates some shapes produced at LMSC.

PROPERTY ANALYSIS

Table 1 is a summary of mechanical, physical, thermal, and electrical properties. These properties are reviewed here to better describe the methods employed and to compare these values with more common materials.

- Density

  Extremely low permeability allows the water displacement method to be used with good accuracy. No appreciable change in density was noted after a 24-hr water soak. The density range is directly related to material thickness; i.e., thin material has low density, thick material has high density. The material density is 20% lower than conventional high density polycrystalline graphite (Ref. 2).

- Crystalline Characteristics

  The basic glassy carbon structure is a combination of tetrahedral and trigonal linkages which are related to the turbostratic precursor polymer structure. No significant degree of structural order has been found even after prolonged heat treatment at 3000°C (Ref. 3). The internal pore structure is unconnected, quite small in size, and uniformly dispersed (Ref. 4).

- Gas Permeability

  These values are extremely low and compare to borosilica glass. No appreciable outgassing under high vacuum conditions has been found in electronics applications. Complex shapes can be fabricated with relative ease to perform high-temperature, high-vacuum work.

- Tensile Strength

  Test specimens employed were 1/8-in.-diameter rods epoxy-bonded into metal tab ends. Rod fabrication does not require special tooling and provides an excellent gauge-length surface. The fracture surface is

Table 1

LMSC GLASSY CARBON PROPERTY DATA

Property	Test Method	Material Grade	
		2000	3000
Density (g/cm^3)	ASTM D-792 Method A	1.43 – 1.50	1.36 – 1.42
Crystalline Characteristics	X-ray diffraction		
L_c, Å		19	110
d, Å		3.56	3.45
Ave. Pore Radius, Å		23	60
Gas Permeability (cm^2/sec)	Helium ΔP - 1 atm	10^{-10} – 10^{-12} (est.)	10^{-7} – 10^{-9} (est.)
Tensile Strength ($lb/in.^2$)	ASTM D-638 1/8-in.-dia. rods	17,000 – 29,000*	15,000 – 29,000*
Flexural Strength ($lb/in.^2$)	ASTM D-790 Short beam 1/8 × 1/4 × 1 in.	18,100 – 22,900*	13,100 – 20,000*
Compressive Strength ($lb/in.^2$)	ASTM D-695	128,000 – 200,000*	86,600 – 150,000*
Young's Modulus (10^{-6} $lb/in.^2$)	ASTM E-111	4.0	3.4
Impact Strength (in.-lb/in. notch)	ASTM D-256 Method C	1.2	1.2
Poisson's Ratio	ASTM E-132	0.12	0.1 (est.)
Shear Modulus (10^6 $lb/in.^2$)	ASTM E-143	1.65	1.4 (est.)
Hardness Vickers	ASTM E-92	200	90 – 160
Thermal Conductivity (cal/cm/°C/sec)	Thermal diffusivity	0.010	0.012
Thermal Expansion (10^{-6}/°C)	ASTM B-95 23° – 1600°C	4.2	5.0
Specific Heat (cal/g/°C)	ASTM C-351	0.18 @ 38°C 0.48 @ 927°C	–
Electrical Resistivity (10^{-4} ohm-cm)	ASTM B-70	168	18

*A-2 series of extra high-strength, glass-like carbons.

smooth and glass-like in appearance. The epoxy-carbon bond is an excellent method of attachment for structural applications. Various grades of material are available. Experimental material (designated as A-2) having tensile strength up to 29,000 psi has been developed. The high-temperature tensile strength of LMSC standard grade 2000 (GW-173), a stock item, is shown in Fig. 1. The experimental material should exhibit similar high-temperature capability.

- <u>Flexural Strength</u>
  The test employed a 3/4 × 1/4 × 1/8 in. short beam specimen, using 3-pt. loading. No deformation at loading points is evident.

- <u>Compressive Strength</u>
  The high compressive strength results in a failure mode that is sudden and reduces the specimen to dust-sized pieces. The compressive modulus appears similar to Young's modulus, linear to the ultimate strength.

- <u>Young's Modulus</u>
  Figure 2 is a typical stress-strain curve for 2000-grade material tested at 23°C. The material appears to obey Hook's law of linearity to its ultimate strength. Specimens have been stress-cycled with no change in modulus or hysterysis effect.

- <u>Impact Strength</u>
  The Izod notch test indicates a close similarity to conventional carbons and graphites.

- <u>Poisson's Ratio</u>
  As expected, transverse strain is also quite linear and the modulus does not change after repeated load cycles.

- <u>Shear Modulus</u>
  This value was calculated from Poisson's ratio.

- <u>Hardness, Vickers</u>
  Grade 2000 material is hard enough to scratch soda glass. The procedure for machining is similar to that for glass and ceramics, requiring a

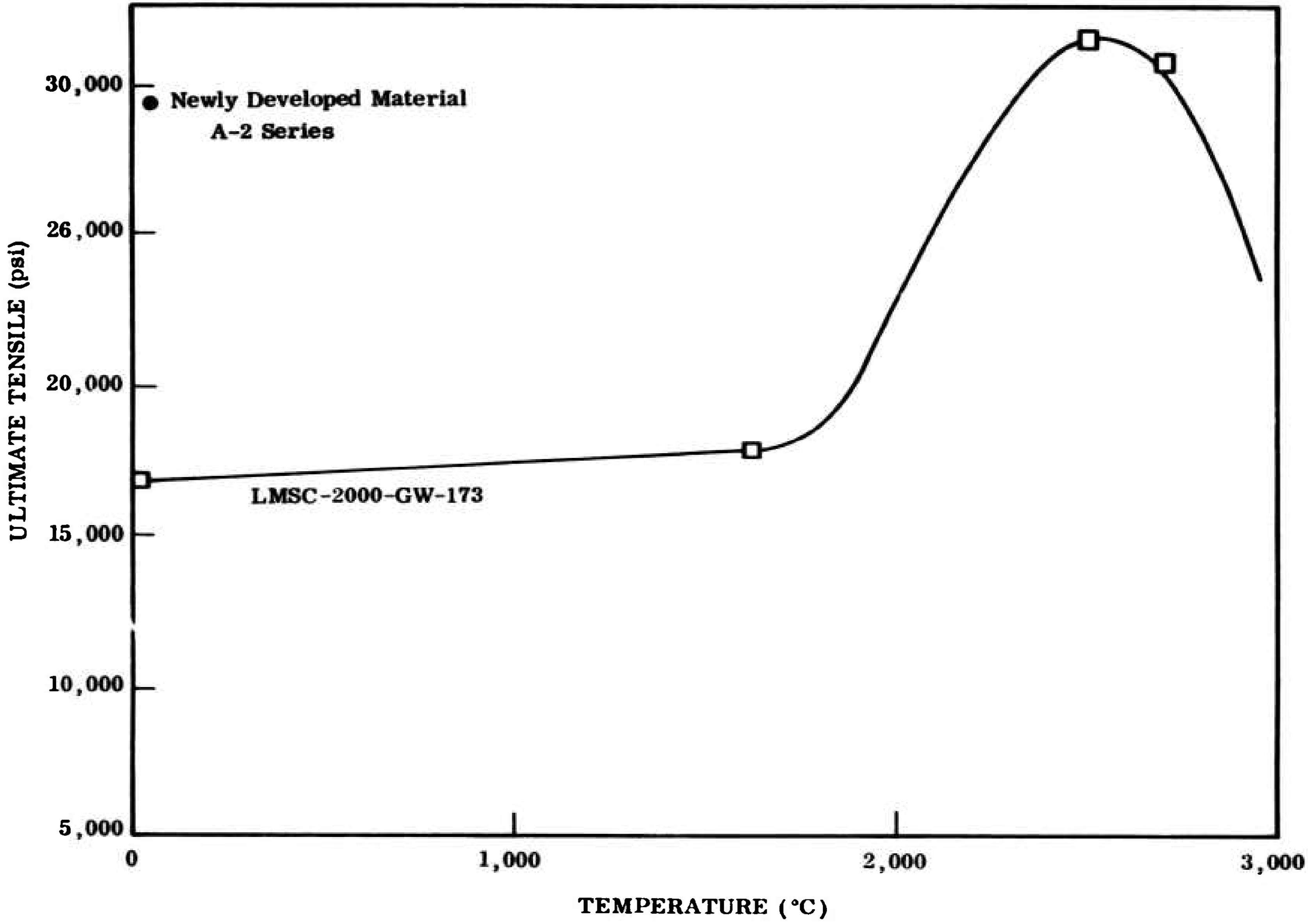


Fig. 1 Tensile Strength of LMSC Glass-Like Carbon

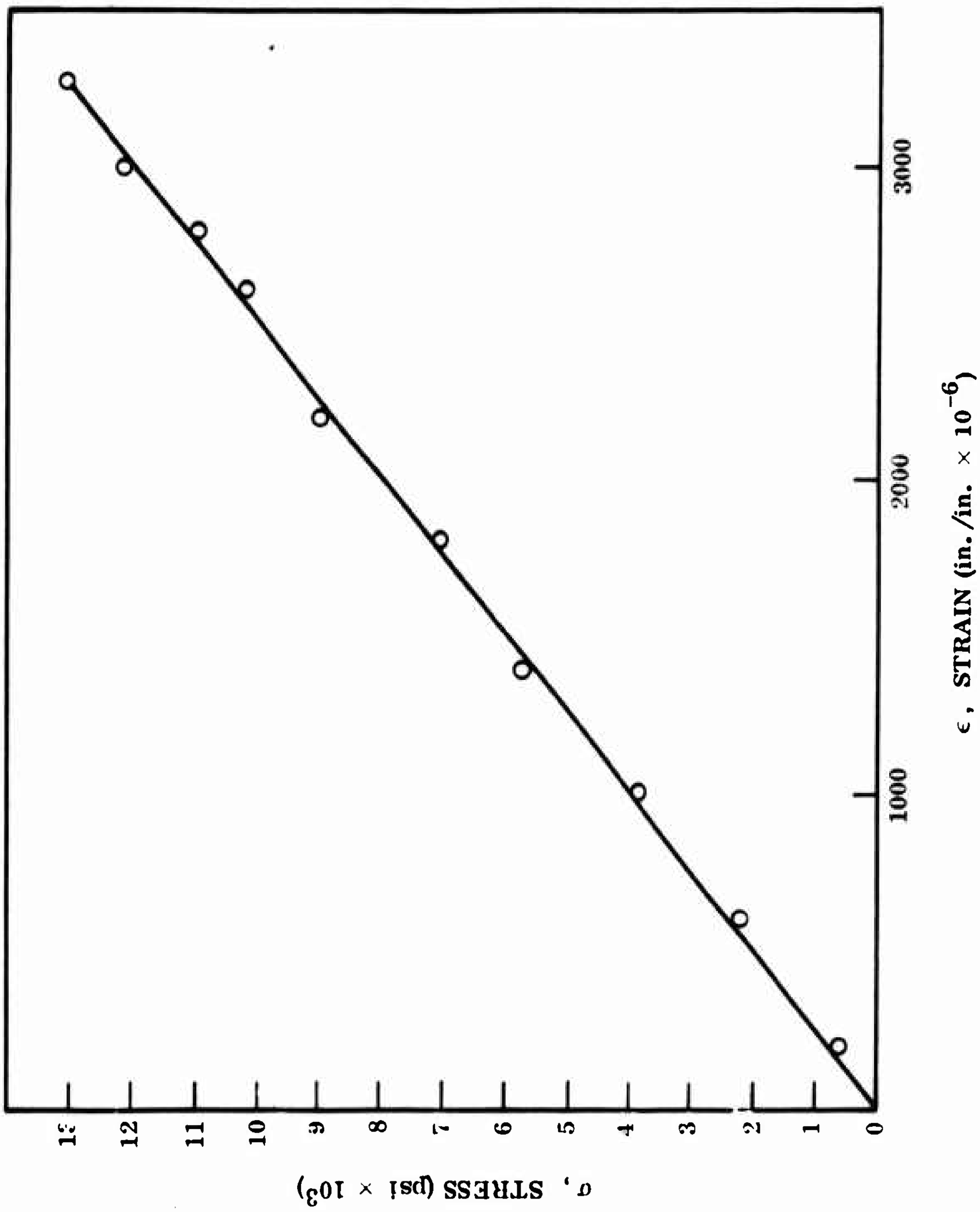


Fig. 2 Typical Stress-Strain Curve for 2000-Grade Material

diamond or carbide-faced cutting tool. Preferably, shapes are produced net to eliminate the necessity of additional machining.

- Thermal Conductivity
  The thermal conductivity of the conventional grades of glass-like carbon are about 1/10 that of conventional high density polycrystalline graphites.

- Thermal Expansion
  Thermal expansion versus temperature is presented in Fig. 3. This curve appears very similar to experimental data for ATJ-S graphite (across grain) and a little higher than ATJ-S with grain.

- Specific Heat
  These values appear similar to conventional carbons and graphites.

- Electrical Resistivity
  Coils and exotic shapes can be produced to allow for thermal expansion stresses. Considerable freedom is available to design a superior resistance element or induction susceptor.

- Other Properties
  Many properties cannot be related to a meaningful standard test.
  - Oxidation resistance studies indicate similar or much lower surface recession when compared to conventional carbons and graphites. Ablation is extremely even with no spallation. Figure 4 compares conventional, high-density, polycrystalline graphite with LMSC Glass-Like Carbon under cold air, hot specimen conditions.
  - Cryogenic sensitivity was studied by repeated exposure to liquid nitrogen. No detrimental effects were noted.
  - Thermal shock sensitivity is not a problem for general applications provided it is handled like a ceramic. In testing for reentry applications, best results were obtained with the 3000-grade material coupled with a substructure of higher thermal conductivity.

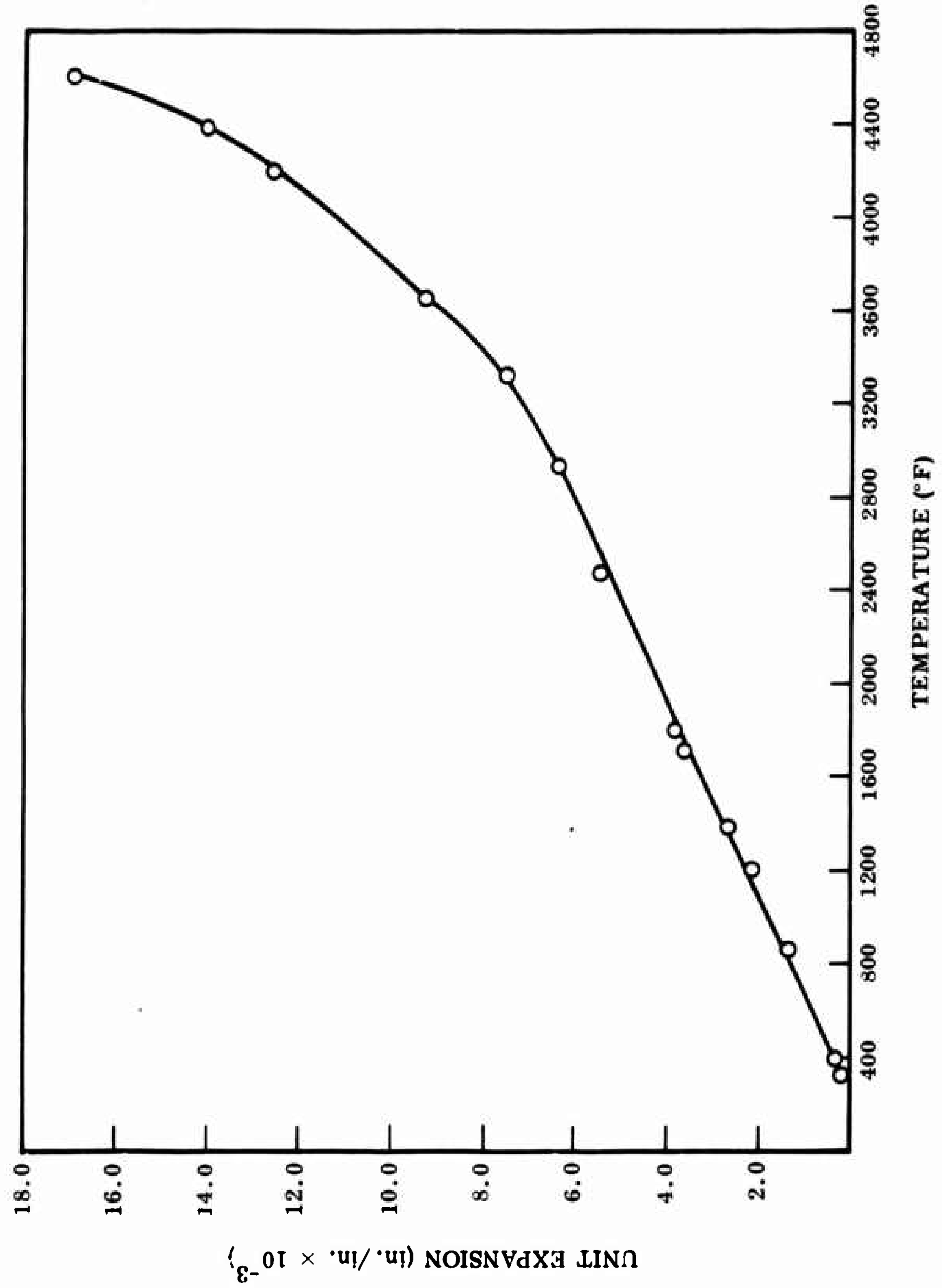


Fig. 3 Thermal Expansion of 2000-Grade LMSC Glass-Like Carbon

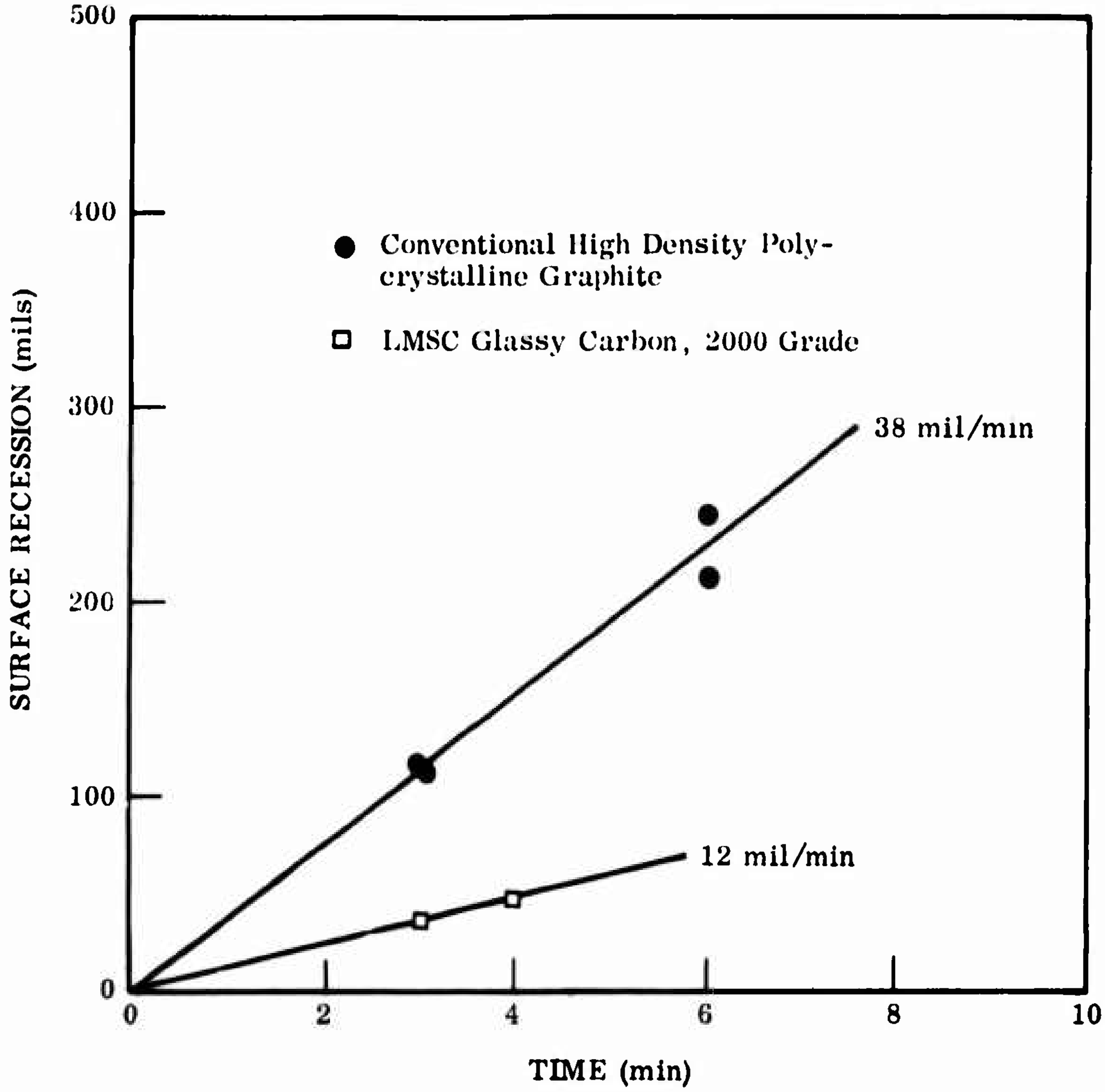
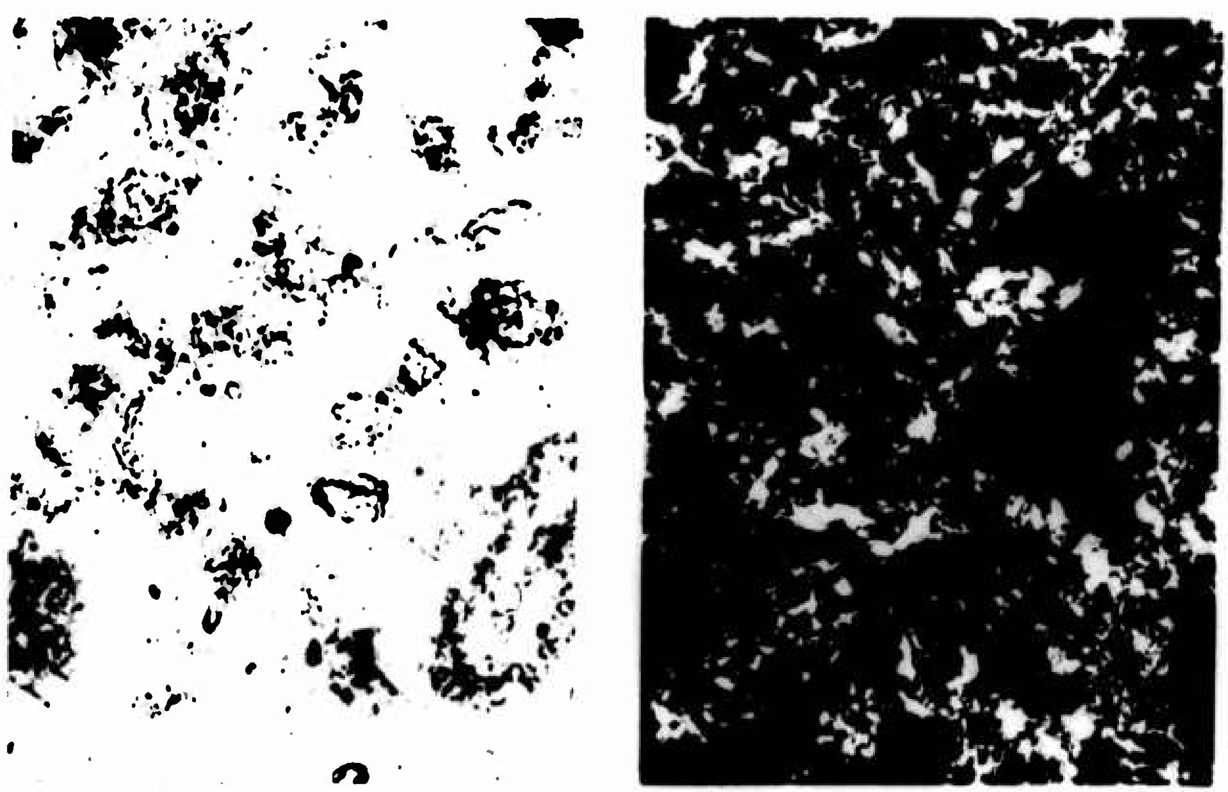


Fig. 4 Flat Face Cylinder, 3000°F, 50 fps

GLASS-LIKE CARBON MODIFIED FOR HIGH THERMAL CONDUCTIVITY

A special form of graphite-modified glass-like carbon was developed (Ref. 5) for certain applications such as extremely severe hyperthermal environments. These materials are also suitable for applications requiring higher electrical resistivity and higher lubricity.

These materials can be obtained in thicknesses somewhat greater than conventional glassy carbon. Typical microstructure is shown in Fig. 5.



Bright Field 500×   Polarized Light 500×

Fig. 5 Microstructure of Graphite-Filled LMSC Glass-Like Carbon

The properties of the modified form of glassy carbon are compared with that of conventional graphite in Table 2. As indicated, the thermal conductivity is increased by a factor of 10. This results in an order-of-magnitude increase in the thermal shock parameter. There is some decrease in static mechanical properties; however, there is an increase in the percent strain to failure which improves the dynamic performance of the material. Stress cycling produced a hysteresis and modulus reduction in the stress-strain curve. A reduction in modulus is desirable from the stand-point of thermal shock.

Table 2

PROPERTIES OF CONVENTIONAL VERSUS MODIFIED GLASS-LIKE CARBON

Property	Conventional Glassy Carbon	Modified Glass-Like Carbon*
Heat Treatment Temperature	2,000	2,500
Density	1.45	1.56
Tensile Strength (psi), S	17,000	8,600
Flexural Strength (psi)	18,100	6,600
Compressive Strength (psi)	150,000	26,600
Thermal Conductivity ($cal/cm^2 \cdot {}^\circ C \cdot sec$)	0.010	0.112
Young's Modulus, E	4.0	1.4
Poisson's Ratio, μ	0.12	0.10
Thermal Expansion, α ($10^{-6}/{}^\circ C$)	3.4	3.0 est.
$R = \frac{S}{E}\,(1-u).\frac{K}{\alpha}$ ($Btu/hr/ft^2/in.$)	0.0375	0.485

*20 vol% graphite additive.

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